

TEXT SEARCHABLE DOCUMENT - 2010

Data Evaluation Record on the adsorption-desorption of dimethyl disulfide in soil

PMRA Submission Number {.....}

EPA MRID Number 46917014

Data Requirement: PMRA Data Code:
EPA DP Barcode: D332939
OECD Data Point:
EPA Guideline: 163-1

Test material:

Common name: Dimethyl disulfide.
Chemical name:
IUPAC name: Dimethyl disulfide.
CAS name: Not reported.
CAS No.: 624-92-0.
Synonyms: Dimethyldisulfide; DMDS; 2,3-dithiabutane; methyl disulfide;
(methyldithio)methane; (methylsulfanyl)methane; methyldithion ethane.
Smiles string: S(SC)C (EPI Suite, v3.12 SMILES String).

Primary Reviewer: Amy Barnes
Cambridge Environmental

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05/12/10

Company Code:
Active Code:
Use Site Category:
EPA PC Code: 029088

CITATION: Völkel, W. 2006. Adsorption/desorption of DMDS on one soil. Unpublished study performed by RCC Ltd, Itingen, Switzerland; sponsored by Cerexagri S.A., Plaisir, France and Arkema, Paris, France; and submitted by Cerexagri, Inc., King of Prussia, Pennsylvania. RCC Study Number 858327. Experimental start date January 14, 2005, and completion date November 8, 2005 (p. 10). Final report issued June 19, 2006.



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EXECUTIVE SUMMARY

The adsorption/desorption characteristics of [¹⁴C]dimethyl disulfide (DMDS) were studied in a sandy loam soil [pH 7.8, organic carbon 0.6%] from California, USA, in a batch equilibrium experiment. The experiment was conducted in accordance with USEPA Subdivision N, Chemistry: Environmental Fate, Section 163-1: Leaching and Adsorption/Desorption Studies. This study was conducted in compliance with the Swiss Ordinance relating to Good Laboratory Practice. The adsorption phase of the study was carried out by equilibrating gamma-irradiated air-dried soil with [¹⁴C]dimethyl disulfide at analytically measured concentrations of 0.001, 0.002, 0.011, 0.021, and 0.102 mg a.i./kg soil, in the dark at 20 ± 2°C for 24 hours. The equilibrating solution used was 0.01M CaCl₂ solution, purged with helium. The soil solution ratio was 1:1 (w:v). The desorption phase of the study was carried out by replacing the adsorption solution with an equivalent volume of 0.01M CaCl₂ solution and equilibrating in the dark at 20 ± 2°C for 44 hours. One desorption step was performed.

The supernatant solutions after adsorption and the desorption step were separated by centrifugation, and were analyzed for total radioactivity using LSC. Aliquots of the adsorption and desorption supernatants were analyzed for [¹⁴C]dimethyl disulfide using HPLC.

The experimental temperature employed during the study was reported to be maintained at 20 ± 2°C; supporting data were not provided. The pH of samples without soil before application was 6.03. The pH of samples with soil after equilibration was 7.06. Based on HPLC analysis of the adsorption and desorption supernatants, [¹⁴C]dimethyl disulfide degraded, accounting for 93.5% and 58.0% of the radioactivity, respectively. Based on HPLC analysis of the application solution and supernatant of the control solution after 24 hours of shaking, [¹⁴C]dimethyl disulfide had a radiochemical purity of 98.1% and 98.4%, respectively. A mass balance could not be determined from the definitive study.

After 24 hours of equilibration, the study author reported 16.1-47.6% of the applied [¹⁴C]dimethyl disulfide was adsorbed to the sandy loam soil (registrant-calculated). The registrant-calculated Freundlich adsorption K value was 0.071, and the Freundlich K_{oc} value was 12. Registrant-calculated adsorption K and K_{oc} values were not reported. The reviewer calculated Freundlich adsorption K value is 0.083, and the Freundlich K_{oc} value is 89. The reviewer-calculated adsorption K and K_{oc} value is 0.537 and 89 respectively

In the desorption kinetic experiment, a constant decrease of radioactivity in the supernatant was observed. The sandy loam soil averaged 34.0% of the adsorbed after 4 hours, decreased to 20.9% after 24 hours, and was -3.5% after 44 hours. The registrant-calculated Freundlich desorption K and K_{oc} values are 0.497 and 83 respectively. The reviewer-calculated Freundlich desorption K and K_{oc} values are 12.6 and 203 respectively. The reviewer-calculated desorption K and K_{oc} values are 12.6 and 2,103 respectively.

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Results Synopsis:

Soil type: California Sandy loam.
Amount adsorbed: 16.1-47.6% of the applied.
Adsorption K_d : 0.515 (reviewer calculated)
Adsorption K_{oc} : 86 (reviewer calculated)
Freundlich adsorption K: 0.071 (reviewer calculated)
Freundlich adsorption K_{oc} : 12 (reviewer calculated)
Amount desorbed: 5.6-11.5% of adsorbed.
Desorption K_d : 5.319 (reviewer calculated)
Desorption K_{oc} : 887 (reviewer calculated)
Freundlich desorption K: 0.461 (reviewer calculated)
Freundlich desorption K_{oc} : 77 (reviewer calculated)

Study Acceptability: This study is classified as Acceptable. Volatile residues were not trapped in the experimental design. However, material balances exceeded 90 percent in the preliminary experiment in all cases. The study was conducted using only one soil type.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: This study was conducted in accordance with OECD Guideline for Testing of Chemicals No. 106: "Adsorption/Desorption" (2000); and under consideration of European Community Commission Directive 95/36/EC (1995) and Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 163-1: Leaching and Adsorption/Desorption Studies (1982; p. 11). The following significant deviations from the objectives of Subdivision N guidelines were noted:

COMPLIANCE: This study was conducted in compliance with the Swiss Ordinance relating to Good Laboratory Practice (2000; p. 3). Signed and dated No Data Confidentiality, GLP, Quality Assurance statements were provided (pp. 2a-3, 5). A Certificate of Authenticity was not provided.

A. MATERIALS:

1. Test Material [^{14}C]Dimethyl disulfide (DMDS; p. 16).

Chemical Structure: See DER Attachment 1.

Description: Pale yellow liquid, Technical grade (radiolabeled test material, p. 16).

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Purity:

Radiolabeled

Radiochemical purity: >99% (Batch I); 98.7% (Batch II; p. 16).

Lot No.: 040401 (RCC No. 156096/A; Batch I)
49520-1-4C (RCC No. 162945/A; Batch II).

Analytical purity: Not reported.

Specific radioactivity: 392 $\mu\text{Ci}/\text{mg}$ (14.5 MBq/mg).

22.8 $\mu\text{Ci}/\text{mMol}$ (8.96 MBq/mg).
(740 Mbq; Batch II).

Location of the label: Labeled on both carbons of the molecule.

Storage conditions of test chemicals:

Radiolabeled test substance was stored at *ca.* -20°C at RCC Ltd. and at <0°C at the sponsor facility (p. 16).

Physico-chemical properties of dimethyl disulfide:

Parameter	Value	Comment
Molecular weight	Not reported.	
Molecular formula	$\text{C}_2\text{H}_6\text{S}_2$	
Water Solubility	Not reported.	
Vapor Pressure/Volatility	28.6 mm Hg (DMDS)/ 121.6 mm Hg (hexane).	At 25°C.
UV Absorption	Not reported.	
pKa	Not reported.	
$K_{ow}/\log K_{ow}$	Not reported.	
$\log P_{ow}$	1.77.	
Specific gravity ($\text{H}_2\text{O} = 1$)	<1	
Stability of compound at room temperature, if provided	Stable under normal conditions.	

Data were obtained from pp. 16-17; Figure 9, p. 54 of the study report.

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2. Soil Characteristics

Table 1: Description of soil collection and storage.

Description	Sandy loam
Geographic location	California, USA
Pesticide use history at the collection site	Not reported.
Collection procedures	Not reported.
Sampling depth (cm)	Not reported.
Storage conditions	Not reported.
Storage length	Not reported.
Soil preparation	Air-dried and sieved (2 mm); sterilized by gamma radiation.

Data were obtained from pp. 17-18 and Table 1, p. 33 of the study report.

Table 2: Properties of the soils.

Property	California
Soil texture (USDA)	Sandy loam
% Sand (>0.05 mm)	71
% Silt (0.002-0.05 mm)	16
% Clay (<0.002 mm)	13
pH (1:1 soil water ratio)	7.8
Organic carbon (g/100 g soil)%	0.6
Organic matter (Walkley Black)	1.0
CEC (meq/100 g soil)	8.9
CaCO ₃ (%)	Not reported.
Moisture at 1/3 atm (%)	Not reported.
Bulk density (g/cm ³)	1.27
Biomass (mg microbial C/100 g or CFU or other)	Not reported.
Soil taxonomic classification	Not reported.
Soil mapping unit (for EPA)	Not reported.

Data were obtained from Table 1, p. 33 of the study report.

Soil bulk density provided by registrant in confirmatory e-mail.

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C. STUDY DESIGN:

1. Preliminary study: Preliminary experiments were conducted to determine the appropriate soil:solution ratio and equilibrium times and adsorption of the test material to the test vessels, and to assure the stability of the test compound during selected exposure time to be used in the definitive study (p. 18).

Prior to study initiation, stock solutions were prepared for the preliminary experiments by mixing [¹⁴C]dimethyl disulfide (in hexane) with ethanol (p. 19). Aliquots were analyzed for total radioactivity using LSC.

To determine the soil:solution ratio, 2 x 4.0, 7.2 or 15.0 g of the California sandy loam test soil were added into headspace vials and suspended in *ca.* 20.0, 18.0 or 15.0 mL of 0.01M CaCl₂ solution, resulting in soil:solution ratios of 1:5, 1:2.5, and 1:1 (w:v; pp. 18-19). The samples were sealed with crimp-caps equipped with septa, and pre-equilibrated by shaking for *ca.* 12 hours in the dark at 20 ± 2°C (p. 17). Following pre-equilibration, the samples were treated with 66, 59 or 50 µL of [¹⁴C]dimethyl disulfide stock solution at a nominal test concentration of 0.06 mg/L (p. 21). The samples were shaken for 48 hours. Following shaking, the samples were centrifuged and duplicate aliquots of the supernatants were analyzed for total radioactivity using LSC. Aliquots of the supernatants were analyzed using HPLC. Selected samples at the 1:1 (w:v) soil:solution ratio were analyzed for mass balance. The remaining soil was extracted three times with acetonitrile (10 mL; p. 22). The extracts were combined and quantified by LSC. Following extraction, the samples were combusted. After 48 hours, adsorption averaged 79.4%, 14.6%, and 3.0% at soil:solution ratios of 1:1, 1:2.5, and 1:5 (w:v), respectively (p. 28; Table 2, p. 34). The test compound was not stable over 48 hours (Figure 8, p. 53). The mass balance averaged 95.4% (range 94.2-96.7%) of the applied (Table 3, p. 35).

Treated aqueous samples without soil were exposed for 48 hours and analyzed by LSC to determine glass adsorption and stability (p. 20). Additional aliquots were analyzed using HPLC performed under the following conditions (p. 23): Merck Li-Chrospher 100 RP18 pre-column (4 x 4 mm; 5 µm particle size), Nucleosil C-18 column (4.6 x 250 mm; 5 µm particle size), mobile phase combining (Solvent A) water and (Solvent B) acetonitrile [percent A:B (v:v) at 0 min., 75:25; 15 min., 0:100; 20 min., 0:100; 20.1 min., 75:25; 35 min., 75:25], flow rate of 1 mL/minute, using a FLO-ONE Beta A500 or 500 TR detector. [¹⁴C]Dimethyl disulfide was identified by comparison to the retention time of an unlabeled reference standard (R_t = *ca.* 11.5-13.30 min.; Figures 8-10, pp. 53-55). It was determined that [¹⁴C]dimethyl disulfide was not stable (p. 28; Figure 8, p. 53). In addition, no significant adsorption of the test material to the vessels was observed, with [¹⁴C]dimethyl disulfide accounting for 100.7% of the applied (Table 2, p. 34).

To determine the adsorption equilibration time, 2 x 11.0 g of gamma-irradiated test soil were added into headspace vials and suspended in *ca.* 16.5 mL of 0.01M CaCl₂ solution (p. 19). The samples were sealed with crimped-caps equipped with septa, and pre-equilibrated by shaking for *ca.* 12 hours in the dark at 20 ± 2°C (pp. 17-18). Following pre-equilibration, the samples were treated with a 90-µL aliquot of [¹⁴C]dimethyl disulfide stock solution at a nominal test

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concentration of 0.1 mg/L. The samples were shaken for 2, 5, 24, and 48 hours (p. 21). Following each sampling interval, the samples were centrifuged and duplicate aliquots of the supernatants were analyzed for total radioactivity using LSC. Controls (treated aqueous samples without soil) were assayed the same way as the treated samples. Additional samples were analyzed using HPLC as previously described. Following adsorption, selected samples were analyzed for mass balance and the soils were extracted and combusted as described above. Steady state conditions were reached between 5 and 24 hours (p. 29). After 24 hours, adsorption averaged 9.3% of the applied (Table 4, p. 36; Figure 1, p. 46). No adsorption of the test item onto the surface of the test vessels was observed. After 48 hours, the material balance averaged 100.8% (range 100.3-101.2%) of the applied (Table 5, p. 37). HPLC analysis of the supernatant and extracts showed that the test item was stable (purity 97.0% and 100%, respectively; Figure 10, p. 55). Following 48 hours of adsorption, the K_d and K_{oc} values averaged 0.2 mL/g and 42 mL/g, respectively (Table 6, p. 38).

Based on the results of the preliminary studies, it was determined that the definitive study would be conducted using an equilibration time of 24 hours and a soil:solution ratio of 1:1 (w:v; p. 29). It was also determined to sterilize the test soils for the definitive study using gamma irradiation due to instability of the test substance.

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2. Definitive study experimental conditions:

Table 3: Study design for the adsorption phase.

Parameters		California Sandy loam
Condition of soil (air dried/fresh)		Air-dried; sterilized using gamma radiation. ¹
Have these soils been used for other laboratory studies? (specify which)		No
Soil (g/replicate)		14.5
Equilibrium solution used (eg: 0.01N CaCl ₂)		0.01M CaCl ₂ ; flushed with helium gas.
Control used (with salt solution only) (Yes/No)		Yes.
Test material concentrations ²	Nominal application rates (mg a.i./kg soil)	Not reported.
	Analytically measured concentrations (mg a.i./kg soil)	0.001, 0.002, 0.011, 0.021, 0.102
Identity and concentration of co-solvent, if any		Ethanol., concentration not reported.
Soil:solution ratio (w:v)		1:1
Initial pH of the equilibration solution, if provided		6.03
No. of replications	Controls	Duplicate.
	Treatments	Duplicate.
Equilibration	Time (hours)	24
	Temperature (°C)	20 ± 2°C
	Darkness (Yes/No)	Yes.
	Shaking method	Rotary shaker.
	Shaking time (hours)	24
Method of separation of supernatant (eg., centrifugation)		Centrifugation.
Centrifugation	Speed (rpm)	2800
	Duration (min)	10
	Method of separation of soil and solution	Not reported.

Data were obtained from pp. 17-21; Table 13, p. 45 of the study report.

1 The test soils were equilibrated with CaCl₂ solution, purged with helium, for 12 hours prior to use.

2 Test material concentrations were calculated by the reviewer by converting mg/L to mg a.i./kg using the following equation: [test concentration (mg/L) × total volume of test material (mL)] ÷ amount of soil (g); eg. For the California sandy loam, highest concentration: [0.102 mg/L × 14.5 mL] ÷ 14.5 g = 0.102 mg a.i./kg soil.

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Table 4: Study design for the desorption phase.

Parameters		California Sandy loam
Were the soil residues from the adsorption phase used? If not, describe the method for adsorption using a separate adsorption		Yes.
Amount of test material present in the adsorbed state/adsorbed amount (mg a.i./kg soil)	0.001	0.0005
	0.002	0.0010
	0.011	0.0022
	0.021	0.0040
	0.102	0.0164
No. of desorption steps		1
Equilibration solution and quantity used per treatment for desorption (eg., 0.01M CaCl ₂)		0.01M CaCl ₂ , flushed with helium gas; ca. 14.5 mL.
Soil:solution ratio (w:v)		1:1
Replications	Controls	Duplicate.
	Treatments	Duplicate.
Desorption equilibration	Time (hours)	44
	Temperature (°C)	20 ± 2°C
	Darkness	Yes.
	Shaking method	Rotary shaker.
	Shaking time (hours)	44
Centrifugation	Speed (rpm)	2800
	Duration (min)	10
	Method of separation of soil and solution	Not reported.

Data were obtained from pp. 20-22 and Table 7, p. 39 of the study report.

Desorption Kinetics: The desorption kinetic experiment was carried out at a soil:solution ratio of 1:1 (w:v) and the highest test concentration. Following 24 hours of adsorption, the supernatant was removed and replaced with an equivalent volume of CaCl₂ solution that had been purged with helium, and a desorption phase was conducted (p. 22). After 4, 24, and 44 hours of desorption, duplicate aliquots were analyzed by LSC. Aliquots of the supernatants were analyzed using HPLC after 44 hours to check stability of the test substance.

3. Description of analytical procedures:

Extraction/clean up/concentration methods: No extraction/clean up/concentration methods were employed in this study.

Total [¹⁴C] measurement: Following the adsorption and desorption phases, duplicate aliquots of the supernatants were analyzed for total radioactivity using LSC (p. 20, 22). The amount of the test item absorbed was determined from the difference between the initial and final amount in the aqueous phase (p. 21).

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Non-extractable residues, if any: No non-extractable residues were determined in this study.

Derivatization method, if used: A derivatization method was not employed in this study.

Identification and quantification of parent compound: Following adsorption and desorption, aliquots were analyzed by HPLC under the following conditions (p. 23): Merck Li-Chrospher 100 RP18 pre-column (4 x 4 mm; 5 μ m particle size), Nucleosil C-18 column (4.6 x 250 mm; 5 μ m particle size), mobile phase combining (Solvent A) water and (Solvent B) acetonitrile [percent A:B (v:v) at 0 min., 75:25; 15 min., 0:100; 20 min., 0:100; 20.1 min., 75:25; 35 min., 75:25], flow rate of 1 mL/minute, using a FLO-ONE Beta A500 or 500TR detector. [¹⁴C]Dimethyl disulfide was identified by comparison to the retention time of an unlabeled reference standard (Rt = ca. 13.00 min; Figure 12, p. 57).

Identification and quantification of transformation products, if appropriate: Samples were not analyzed for transformation products of dimethyl disulfide.

Detection limits (LOD, LOQ) for the parent compound: For LSC analysis, the Limits of Detection (LOD) were 0.16%, 0.15%, and 0.26% of the applied for the aqueous phase, soil extracts, and combustion non-extractables, respectively (corresponding to 0.002 μ g, 0.002 μ g, and 0.004 μ g parent equivalents; Appendix I, pp. 59-60). The corresponding LSC Limits of Quantification (LOQ) were 0.24%, 0.22%, and 0.39% of the applied (corresponding to 0.004 μ g, 0.003 μ g, and 0.006 μ g parent equivalents). For HPLC analysis, the LOQ was 1.1% of the applied. The LOD was not reported.

Detection limits (LOD, LOQ) for the transformation products, if appropriate: Samples were not analyzed for transformation products of dimethyl disulfide.

II. RESULTS AND DISCUSSION

A. TEST CONDITIONS: The experimental temperature employed during the study was reported to be maintained at $20 \pm 2^\circ\text{C}$; supporting data were not provided (p. 17). The pH of samples without soil before application was 6.03. The pH of samples with soil after equilibration was 7.06 (Table 13, p. 45). Based on HPLC analysis of the adsorption and desorption supernatants, [¹⁴C]dimethyl disulfide degraded, accounting for 93.5% and 58.0% of the radioactivity, respectively (pp. 29-30; Figure 12, p. 57). Based on HPLC analysis of the application solution and supernatant of the control solution after 24 hours of shaking, [¹⁴C]dimethyl disulfide had a radiochemical purity of 98.1% and 98.4%, respectively (p. 28; Figure 11, p. 56).

B. MASS BALANCE: Mass balances were not determined in the definitive study. A mass balance was not able to be calculated due to insufficient data. An initial mass from the experimental aliquot solution was not provided to determine the total recovery in the system.

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Table 5: Recovery of [¹⁴C]dimethyl disulfide, expressed as percentage of applied radioactivity, in soil after adsorption/desorption (mean ± s.d.)¹.

Matrices	California Sandy loam
At the end of the adsorption phase	
Supernatant solution	
Solid phase (extracted)	
Non-extractable residues in soil, if measured	
Total recovery	
At the end of the desorption phase	
Supernatant solution	
Washings	
Solid phase (total ¹⁴ C)	
Non-extractable residues in soil, if measured	
Total recovery	

¹ Mass balances were not determined in the definitive experiment.

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Table 6: Concentration of [¹⁴C]dimethyl disulfide in the solid and liquid phases at the end of adsorption equilibration period (mean; n = 2).

Concentration (mg a.i./kg soil)	California Sandy loam		
	on soil (mg a.i./kg)	in solution (µg a.i./mL)	% adsorbed
0.001	0.0005	0.0006	44.5
0.002	0.0010	0.0010	47.6
0.011	0.0022	0.0078	21.2
0.021	0.0040	0.0158	19.1
0.102	0.0164	0.0798	16.1

- 1 Data were obtained from Table 7, p. 39 of the study report. Means were determined by the study author.
- 2 Initial mass of [¹⁴C] DMDS from the experimental aliquot solution is needed to verify the percent adsorbed.

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Table 7: Concentration of [¹⁴C]dimethyl disulfide in the solid and liquid phases at the end of desorption step (mean, n = 2).

Concentration (mg a.i./kg soil)	California Sandy loam		
	on soil (mg a.i./kg)	in solution (µg a.i./mL)	% desorbed as % of the adsorbed
0.001	0.0005	0.0001	Not determined.
0.002	0.0011	0.0001	Not determined.
0.011	0.0036	0.0006	Not determined.
0.021	0.0055	0.0019	Not determined.
0.102	0.0199	0.0117	Not determined.

1. Data were obtained from Table 11, p. 43 of the study report. Means were determined by the study author.
2. Initial mass of [¹⁴C] DMDS from the experimental aliquot solution is needed to verify the percent adsorbed.

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Table 8: Reviewer calculated adsorption and desorption constants of [¹⁴C]dimethyl disulfide in the soils.¹

Soil	Adsorption						Desorption					
	K _d	K _f	1/n	r ²	K _{oc}	K _{foc}	K _d	K _f	1/n	r ²	K _{oc}	K _{foc}
California Sandy loam	0.537	0.083	0.66	0.969	89	14	12.6	1.27	0.68	0.950	2103	203

K_d - Adsorption and desorption coefficients; K_f - Freundlich adsorption and desorption coefficients; 1/n - Slope of Freundlich adsorption/desorption isotherms.

K_{oc} - Coefficient adsorption per organic carbon (K_d or K x 100/% organic carbon).

r² - Regression coefficient of Freundlich equation.

NR = Not reported.

Table 9: Registrant calculated adsorption and desorption constants of [¹⁴C]dimethyl disulfide in the soils.¹

Soil	Adsorption						Desorption					
	K _d	K _f	1/n	r ²	K _{oc}	K _{foc}	K _d	K _f	1/n	r ²	K _{oc}	K _{foc}
California Sandy loam	NR	0.071	0.66	0.9723	86	12	NR	0.497	0.71	0.9789	NR	83

K_{oc} values for each soil were determined based on the mean of K_{oc} values for each sample in Table 7, pp. 39.

Data were obtained from p. 30; Tables 9, 12, pp. 41, 44; and Figures 3-4, 6-7, pp. 48-49, 51-52 of the study report.

K_d - Adsorption and desorption coefficients; K_f - Freundlich adsorption and desorption coefficients; 1/n - Slope of Freundlich adsorption/desorption isotherms.

K_{oc} - Coefficient adsorption per organic carbon (K_d or K x 100/% organic carbon).

r² - Regression coefficient of Freundlich equation.

NR = Not reported.

¹ Freundlich K_f values were calculated by the study author using the following equation (pp. 25-26):

$$\log(C_s) = \log K_f + (1/n) \log(C_{aq}), \text{ where}$$

C_s = soil concentration after adsorption or desorption (µg/g);

C_{aq} = concentration of supernatant after adsorption or desorption (µg/g);

1/n = exponential constant or slope; and

K = Freundlich sorption constant.

C. ADSORPTION: After 24 hours of equilibration, 16.1-47.6% of the applied [¹⁴C]dimethyl disulfide was adsorbed to the California sandy loam soil (registrant-calculated; p. 29; Table 7, p. 39). The registrant-calculated Freundlich adsorption K value was 0.071, and the corresponding Freundlich K_{oc} value was 12 (p. 30; Table 9, p. 41; Figures 3-4, pp. 48-49). Registrant-calculated adsorption K and K_{oc} values were not reported.

The reviewer calculated Freundlich K and K_d values for both the adsorption and desorption phases. The below equations show the calculations of K_f and K_d and subsequent K_{foc} and K_{oc} values.

Freundlich Adsorption and Desorption K_f Value Calculation:

$$K_f = \frac{C_o V_o - C_{eq} V_o}{m} \div C_{eq}^{1/n}$$

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Adsorption and Desorption K_d Value Calculation:

$$K_d = \frac{C_o V_o - C_{eq} V_o}{m} \div C_{eq}$$

Freundlich Adsorption K_f Value Normalized to Organic Carbon Content (K_{foc}) Calculation:

$$K_{foc} = \frac{K_f}{\%OC}$$

Adsorption K_d Value Normalized to Organic Carbon Content (K_{oc}) Calculation:

$$K_{oc} = \frac{K_d}{\%OC}$$

where

C_o = the concentration in the water before sorption ($\mu\text{g/mL}$);;

V_o = the total water volume in the batch system (ml);

m = the dry mass of sorbent (g);

$\% OC$ = percent organic carbon in the soil; and

$1/n$ = exponent of the Freundlich isotherm.

After 24 hours of equilibration, the study author reported 16.1-47.6% of the applied [^{14}C]dimethyl disulfide was adsorbed to the sandy loam soil (registrant-calculated). The reviewer calculated values values were similar to the registrant's provided values for all partition coefficients. The equations shown in II.C were used for these calculations. The registrant-calculated Freundlich adsorption K value was 0.071, and the Freundlich K_{oc} value was 12. Registrant-calculated adsorption K and K_{oc} values were not reported. The reviewer calculated Freundlich adsorption K value is 0.083, and the Freudlich K_{oc} value is 89. The reviewer-calculated adsorption K and K_{oc} value is 0.537 and 89 respectively

The reviewer-calculated r^2 value for Kads vs. $\%$ organic carbon was 0.1441, Kads vs. pH was 4×10^{-5} , and Kads vs. $\%$ clay was 2×10^{-5} . The statistical analysis included the average Kads values and site-specific data for the Speyer, Germany Loam; Mechtildshausen, Germany Loam; Mussig, France Loam; Bretagne, France Silt Loam (MRID 46917015) soil studies and California Sandy Loam soil study (MRID 46917014).

D. DESORPTION: Following the desorption step, the percent of [^{14}C]dimethyl disulfide desorbed from the test soil, as percent of the radioactivity adsorbed, was not determined. The registrant-calculated Freundlich desorption K value for the California sandy loam soil was 0.497 and the corresponding Freundlich desorption K_{oc} value was 83 (p. 30; Table 12, p. 44; Figures 6-7, pp. 51-52). Registrant-calculated desorption K and K_{oc} values were not reported. In the desorption kinetic experiment, there was a constant decrease of radioactivity in the desorption supernatant (Figure 5, p. 50). In the soil pore water of the California sandy loam soil after 24 hours of adsorption, the amount of [^{14}C]dimethyl disulfide desorbed decreased from an average

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34.0% of the adsorbed after 4 hours to 20.9% after 24 hours, and -3.5% after 44 hours (Table 10, p. 42).

In the desorption kinetic experiment, a constant decrease of radioactivity in the supernatant was observed. The sandy loam soil averaged 34.0% of the adsorbed after 4 hours, decreased to 20.9% after 24 hours, and was -3.5% after 44 hours. The reviewer calculated values values were similar to the registrant's provided values for all partition coefficients. The equations shown in II.C were used for these calculations. The registrant-calculated Freundlich desorption K and K_{oc} values are 0.497 and 83 respectively. The reviewer-calculated Freundlich desorption K and K_{oc} values are 12.6 and 203 respectively. The reviewer-calculated desorption K and K_{oc} values are 12.6 and 2,103 respectively.

III. STUDY DEFICIENCIES

1. Material balances were not determined.
2. Volatile residues were not trapped in the experimental design.
3. The study was conducted using only one soil type. Subdivision N guidelines specify that a minimum of four test soils with soil characteristics that are sufficiently different, so as to represent a full spectrum of the types of soil representative of the proposed use areas, be used.

IV. REVIEWER'S COMMENTS

1. The Freundlich $1/n$ values for the adsorption and desorption phases were below 0.9. Freundlich $1/n$ values under idealized conditions should be in the range of 0.9 to 1.1.
2. [^{14}C]Dimethyl disulfide was stable in solution before and after application, based on HPLC analysis of the application solution (purity 98.8% before application and 98.1% after application; p. 28; Figures 9, 11, pp. 54, 56).
3. The maximum field application rate for dimethyl disulfide was not reported. Subdivision N guidelines specify that one test concentration should be roughly equivalent to the maximum proposed or registered field application rate of the parent compound.
4. Registrant values for the indirectly determined concentrations of [^{14}C] DMDS in soil after equilibrium $[(C_oV_o - C_{aq}V_o)/m]$ do not match the reviewer's calculated values.
5. The study author reported incorrectly reported that for the preliminary and screening tests, the aqueous supernatant and the combined extracts of each tube were submitted to HPLC analysis after 24 hours of adsorption (Section 2.3.7, p. 22). The HPLC analyses were conducted after 48 hours of adsorption, based on Table 3 and Figure 8 of the study report (pp. 36, 53).

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V. REFERENCES

1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 163-1. Mobility studies. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-021.
2. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078.
3. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis - Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738.
4. U.S. Environmental Protection Agency. 2003. Guidance for Calculating Sorption Coefficients in Batch Equilibrium Studies.

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Attachment 1: Structures of Parent Compound and Transformation Products

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Dimethyl disulfide [dimethyldisulfide; DMDS; 2,3-dithiabutane; methyl disulfide; (methyldithio)methane; (methyldisulfanyl)methane; methyldithion ethane]

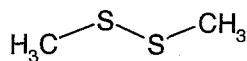
IUPAC Name: Dimethyl disulfide.

CAS Name: Not reported.

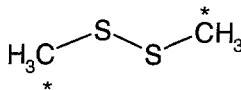
CAS Number: 624-92-0

SMILES String: S(SC)C (EPI Suite, v3.12 SMILES String).

Unlabeled



[¹⁴C]dimethyl disulfide



* = Location of the radiolabel.

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Identified Compounds

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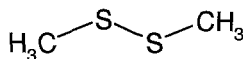
Dimethyl disulfide [dimethyldisulfide; DMDS; 2,3-dithiabutane; methyl disulfide; (methyldithio)methane; (methyldisulfanyl)methane; methyldithion ethane]

IUPAC Name: Dimethyl disulfide.

CAS Name: Not reported.

CAS Number: 624-92-0

SMILES String: S(SC)C (EPI Suite, v3.12 SMILES String).



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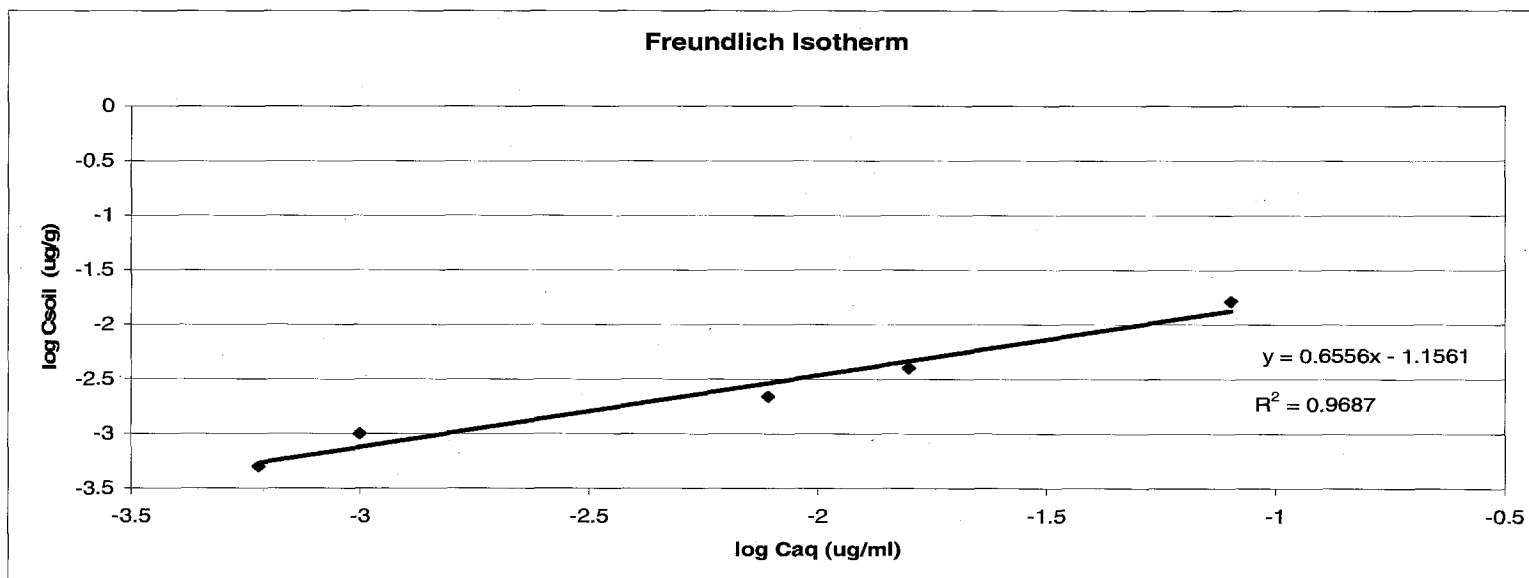
PMRA Submission Number {.....}

EPA MRID Number 46917014

Attachment 2: Excel Spreadsheets

Figure 2-1. Calculation of adsorption soil – water partition coefficients Kd, Koc, Kf, and Kfoc for California Sandy Loam Soil.

C _o Initial Solution Conc. (µg/ml)	C _{soil} Conc. in soil after equilibrium (µg/g)	C _{aq} Conc. in solution after equilibrium (µg/ml)	V _o Volume of Solution (ml)	m Dry mass of sorbent (g)	(C _o V _o - C _{aq} V _o)/m	Kd (ml/g)	OC (%)	Koc (ml/g)	log C _{soil}	log C _{aq}	1/n	Kf (ml/g)	Kfoc (ml/g)
0.102	0.0164	0.0798	14.5	14.5	0.0222	0.278195	0.006	46.36591	-1.785156	-1.097997	0.6556	0.116466	19.41103
0.021	0.004	0.0158	14.5	14.5	0.0052	0.329114	0.006	54.85232	-2.39794	-1.801343	0.6556	0.078879	13.14657
0.011	0.0022	0.0078	14.5	14.5	0.0032	0.410256	0.006	68.37607	-2.657577	-2.107905	0.6556	0.077107	12.85114
0.002	0.001	0.001	14.5	14.5	0.001	1	0.006	166.6667	-3	-3	0.6556	0.09264	15.44005
0.001	0.0005	0.0006	14.5	14.5	0.0004	0.666667	0.006	111.1111	-3.30103	-3.221849	0.6556	0.051797	8.632822
					Σ/n	0.536846		89.47442				0.083378	13.89632

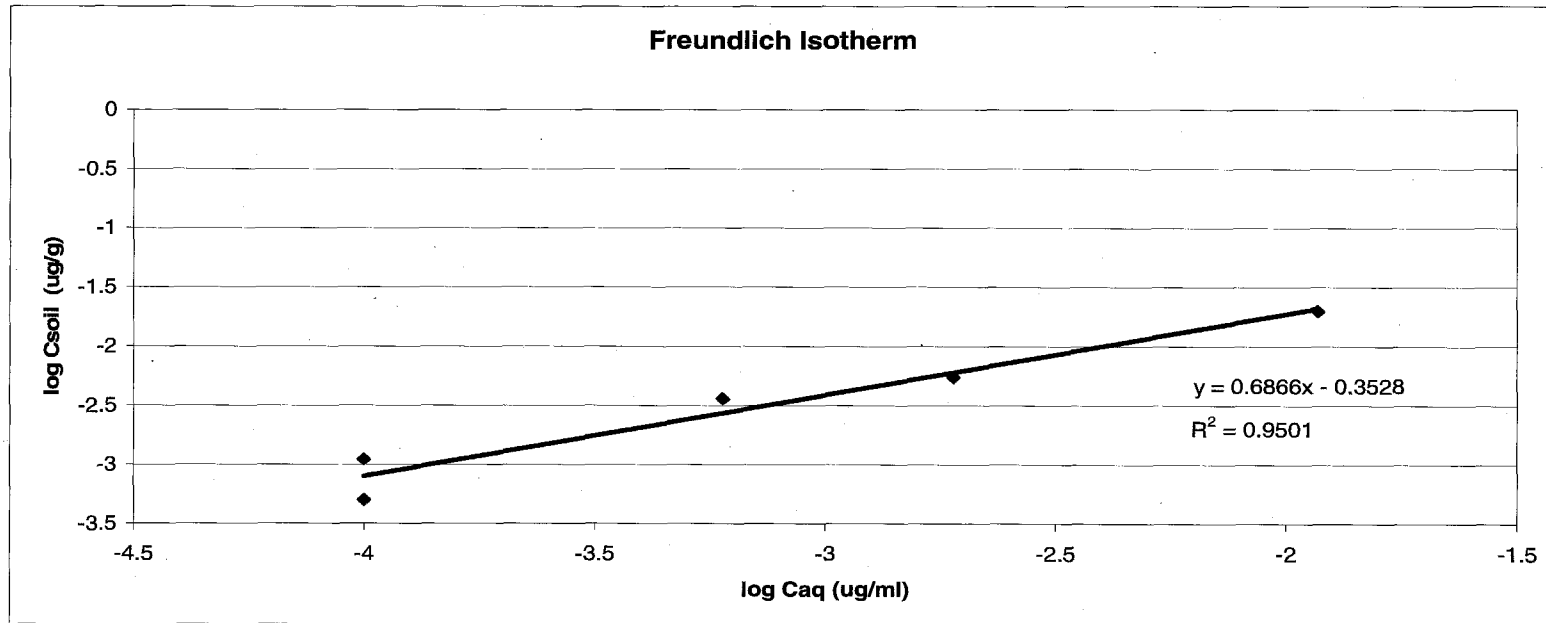


Notes:

1. Data obtained from Table 7, p. 39.
2. C_{soil} and C_{aq} based on registrant-reported mean of two replicates.
3. Registrant only reported the mean C_{soil} and C_{aq} values, but not for individual replicates. Therefore, the C_{soil} and C_{aq} values could not be verified.
4. Registrant reported values of [¹⁴C] DMDS concentrations in soil after equilibrium (shown as C_{soil} above) do not match the calculated values [shown as C_oV_o-C_{aq}V_o/m above].

Figure 2-2. Calculation of desorption soil – water partition coefficients Kd, Koc, Kf, and Kfoc for California Sandy Loam Soil.

C _o Initial Solution Conc. (µg/ml)	C _{soil} Conc. in soil after equilibrium (µg/g)	C _{aq} Conc. in solution after equilibrium (µg/ml)	V _o Volume of Solution (ml)	m Dry mass of sorbent (g)	(C _o V _o - C _{aq} V _o)/m	Kd (ml/g)	OC (%)	Koc (ml/g)	log Csoil	log Caq	1/n	Kf (ml/g)	Kfoc (ml/g)
0.102	0.0199	0.0117	14.5	14.5	0.0903	7.717949	0.006	1286.325	-1.701147	-1.931814	0.6866	1.91457	319.0951
0.021	0.0055	0.0019	14.5	14.5	0.0191	10.05263	0.006	1675.439	-2.259637	-2.721246	0.6866	1.410721	235.1202
0.011	0.0036	0.0006	14.5	14.5	0.0104	17.33333	0.006	2888.889	-2.443697	-3.221849	0.6866	1.694941	282.4902
0.002	0.0011	0.0001	14.5	14.5	0.0019	19	0.006	3166.667	-2.958607	-4	0.6866	1.059628	176.6047
0.001	0.0005	0.0001	14.5	14.5	0.0009	9	0.006	1500	-3.30103	-4	0.6866	0.27885	0.501929
					Σ/n	12.62078		2103.464				1.271742	202.7624

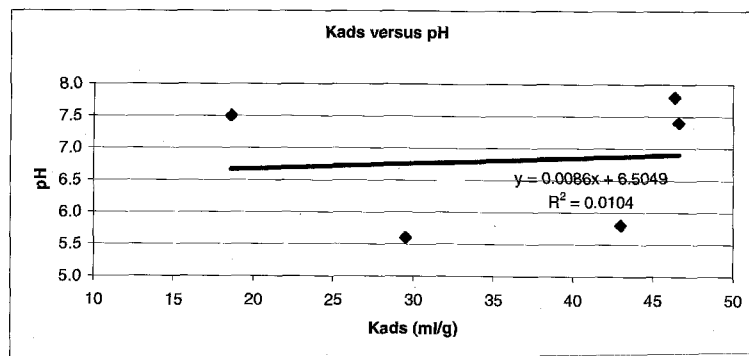
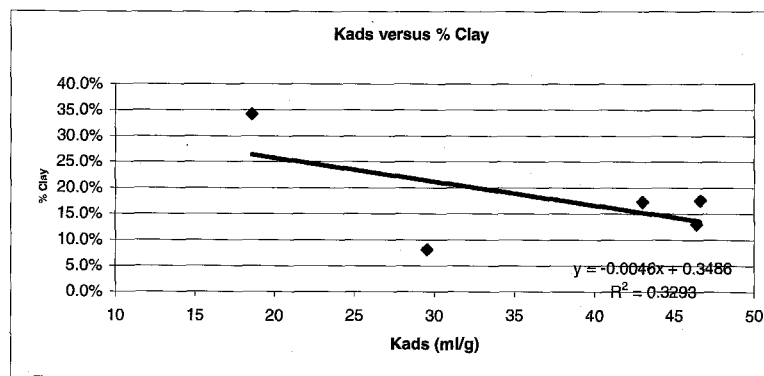
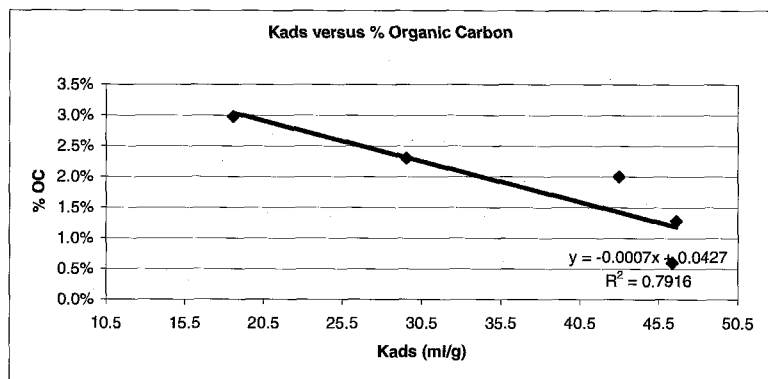


Notes:

1. Data obtained from Table 11, p. 43.
2. Csoil and Caq based on registrant-reported mean of two replicates.
3. Registrant only reported the mean Csoil and Caq values, but not for individual replicates. Therefore, the Csoil and Caq values could not be verified.
4. Registrant reported values of [¹⁴C] DMDS concentrations in soil after equilibrium (shown as C_{soil} above) do not match the calculated values [shown as C_oV_o-C_{aq}V_o/m above].

Figure 2-7. Statistical regression analysis of Kads versus site-specific % organic matter, % clay, and pH from California Sandy Loam; Speyer, Germany Loam; Mechtildshausen, Germany Loam; Mussig, France Loam; and Bretagne, France Silt Loam soil studies.

Soil	Kd (ml/g)	% OC	% Clay	pH
CA Sandy Loam ¹	46.36591	0.006	0.130	7.8
Speyer, GM Sandy Loam ²	29.53888	0.023	0.081	5.6
Mechtildshausen, GM Loam ²	46.62143	0.0128	0.176	7.4
Mussig, FR Clay Loam ²	18.59199	0.0298	0.342	7.5
Bretagne, FR Silt Loam ²	42.99879	0.02	0.174	5.8
Σ/n	36.8234			



Notes:

1. Data were obtained from Table 1, p. 33. Kads values were reviewer-calculated via the direct method using data obtained from Table 11, pp. 43 of the study report (MRID 46917014).
2. Data were obtained from Table 1, p. 35. Kads values were reviewer-calculated via the direct method using data obtained from Table 10, pp. 44-45 of the study report (MRID 46917015).